PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
21.72.WO		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP00/06063	29/06/2000	02/07/1999
International Patent Classification (IPC) or national classification and IPC C09D167/00		
Applicant UCB, S.A.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18/01/2001	01.10.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx. 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Masson, P Telephone No. +49 89 2399 2051

Form PCT IPEA/409 (cover sheet) (January 1994)

ATTACHMENT C

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/06063

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-28 as originally filed

Claims, No.:

1-22 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-22
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-22
Industrial applicability (IA)	Yes:	Claims	1-22
	No:	Claims	

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Cf V:

Reference is made to the following documents:

D1: WO 99 32567 A (MOENS LUC ;BUYSENS KRIS (BE); MAETENS DANIEL (BE); UCB SA (BE)) 1 July 1999 (1999-07-01)

D2: WO 91 14745 A (COURTAULDS COATINGS HOLDINGS) 3 October 1991 (1991-10-03) cited in the application

D3: WO 95 01407 A (EASTMAN CHEM CO) 12 January 1995 (1995-01-12) cited in the application

D4: WO 97 20895 A (UCB SA ;MOENS LUC (BE); MAETENS DANIEL (BE); LOOSEN PATRICK (BE);) 12 June 1997 (1997-06-12) cited in the application

D5: WO 98 47974 A (HEYENK ALBERT ;DSM NV (NL); BESAMUSCA JOHANNES WILHELMUS (NL)) 29 October 1998 (1998-10-29)

Article 33(2) PCT:

None of the documents discloses the same combination of features as disclosed in **claim 1**.

Therefore, the subject matter of **claim 1** meets the requirements of Article 33(2) PCT.

The same considerations apply to the subject matter of the other claims.

Article 33(3) PCT:

Document D3 is considered as representing the closest prior art. The difference between **D3 and claim 1** is that in **D3**, the amorphous carboxylic group containing polyester does not contain any isophthalic moieties as dicarboxylic acid component. The possibility of having an amorphous carboxyl-functional polyester and an semi-crystalline hydroxyl-functional polyester is clearly mentioned in **D3**

(page 4; lines 9 to 15).

There are no comparative examples in the present invention with aliphatic amorphous carboxylic group containing polyester.

Thus, the objective technical problem is to replace in part or entirely the aliphatic diacid units by isophthalic units in the amorphous polyester. **Document D1** indicates that it is known that amorphous carboxylic group containing polyesters which are isophthalic acid rich polyesters can provide thermosetting powder paints and varnishes which have a good outdoor resistance (page 8; lines 14 to 18). Furthermore, the compositions in **accordance with D1** have also good mechanical properties (page 7; lines 6 to 23). **Document D2** teaches that the use of isophthalic acid to make the amorphous polyester in order to obtain a particular resistance to gloss reduction during exposure and also an increased resistance to mechanical deformation (page 1; lines 24 to 27 and lines 28 to 33, page 2; lines 5 to 9 and lines 14 to 17 and page 11; lines 9 to 15). **Document D4** discloses also the use of isophthalic acid as the main acid component for the amorphous carboxylic group containing polyester (page 6; lines 12 to 20 and page 7; lines 9 to 15). Furthermore, the compositions in **accordance with D4** have also good mechanical properties (page 6; lines 12 to 20)

Considering that the aim of the present invention is to have a good weatherability and a good flexibility, there are incentives in the prior art to lead the skilled person to use isophthalic acid as the acid component or the main acid component of the amorphous carboxylic group containing polyester.

Thus, the subject matter of **claim 1** does not meet the requirements of Article 33(3) PCT.

The same considerations apply to the subject matter of **independent claims 19 and 22** as well as to the subject matter of **dependent claims 2 to 18 and 20 to 21** which contain merely conventional embodiments of respectively **claims 1 and 19**.

Article 33(4) PCT:

The subject matter of **all claims** is capable of industrial applicability.

Cf VIII:

In **claim 1**, the expressions "linear or branched carboxylic acid group containing isophthalic acid rich polyester" and "linear or branched hydroxyl group containing polyester" are unclear.

In **claim 1**, the term "isophthalic acid rich group" is a relative term and therefore unclear.

In **claims 3, 4, 6, 7, 8**, the term "etc" introduces an unclarity regarding the list of possible compounds for diacid and glycol components.

In **claims 3, 6 and 7**, the compound "azealic" is unclear.

In **claim 4**, the group of possible compounds for polyacid introduced by the expression "such as" does not limit the scope of this claim. This similar consideration applies also to **claims 5 and 7 to 10**.

In **claim 10**, the expression "wherein one or more of the hydroxyl groups can be hydroxyalkyl substituted" is unclear.

In **claims 11 and 12**, the term "ICI" which relates to viscosity is unclear.

In **claims 16 and 17**, the expression "catalysing amount" is a relative term and therefore renders the subject matter of said claims unclear.

In **claim 18**, the term "substantially" renders the subject matter of this said claim unclear.

ENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
21.72.WO		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP 00/06063	29/06/2000	02/07/1999
Applicant		
UCB, S.A.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ---

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/06063

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D167/00 C09D5/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 32567 A (MOENS LUC ;BUYSENS KRIS (BE); MAETENS DANIEL (BE); UCB SA (BE)) 1 July 1999 (1999-07-01)	
A	WO 91 14745 A (COURTAULDS COATINGS HOLDINGS) 3 October 1991 (1991-10-03) cited in the application	
A	WO 95 01407 A (EASTMAN CHEM CO) 12 January 1995 (1995-01-12) cited in the application	
A	WO 97 20895 A (UCB SA ;MOENS LUC (BE); MAETENS DANIEL (BE); LOOSEN PATRICK (BE);) 12 June 1997 (1997-06-12) cited in the application	

-/--

[X] Further documents are listed in the continuation of box C

[X] Patent family members are listed in annex

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 November 2000	21/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Decocker, L

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/06063

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 47974 A (HEYENK ALBERT ;DSM NV (NL); BESAMUSCA JOHANNES WILHELMUS (NL)) 29 October 1998 (1998-10-29)	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 00/06063

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9932567	A	01-07-1999	BE	1011628 A	09-11-1999
			AU	1744499 A	12-07-1999
			BR	9813617 A	17-10-2000
			EP	1040171 A	04-10-2000
			NO	20003117 A	17-08-2000
			ZA	9811515 A	21-06-1999
WO 9114745	A	03-10-1991	AT	138967 T	15-06-1996
			AU	656890 B	23-02-1995
			AU	7559791 A	21-10-1991
			BR	9106278 A	13-04-1993
			CS	9100811 A	17-12-1991
			DE	69120061 D	11-07-1996
			DE	69120061 T	02-01-1997
			DK	521992 T	14-10-1996
			EP	0521992 A	13-01-1993
			ES	2088493 T	16-08-1996
			GB	2244060 A,B	20-11-1991
			GR	3020671 T	31-10-1996
			HU	62640 A	28-05-1993
			HU	213530 B	28-07-1997
			KR	185652 B	01-05-1999
			PL	166308 B	31-05-1995
WO 9501407	A	12-01-1995	CA	2166306 A	12-01-1995
			EP	0706546 A	17-04-1996
			JP	8512078 T	17-12-1996
			MX	9405012 A	31-01-1995
WO 9720895	A	12-06-1997	BE	1009779 A	05-08-1997
			AU	710516 B	23-09-1999
			AU	1026297 A	27-06-1997
			BR	9611696 A	28-12-1999
			CA	2238435 A	12-06-1997
			CN	1203619 A	30-12-1998
			EP	0865470 A	23-09-1998
			JP	2000501441 T	08-02-2000
			NO	982551 A	05-08-1998
			NZ	323341 A	29-09-1999
			PL	327180 A	23-11-1998
WO 9847974	A	29-10-1998	NL	1005841 C	20-10-1998
			AU	6750898 A	13-11-1998
			BR	9809097 A	01-08-2000
			CN	1260818 T	19-07-2000
			EP	0975701 A	02-02-2000

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 January 2001 (11.01.2001)

PCT

(10) International Publication Number
WO 01/02504 A1

(51) International Patent Classification⁷: C09D 167/00, 5/03

(21) International Application Number: PCT/EP00/06063

(22) International Filing Date: 29 June 2000 (29.06.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99112826.5 2 July 1999 (02.07.1999) EP

(71) Applicant *(for all designated States except US)*: **UCB, S.A.** [BE/BE]; Allée de la Recherche 60, B-1070 Brussels (BE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **MOENS, Luc, Ph., D.** [BE/BE]; Ijsvogellaan 30, B-1640 Sint-Genesius-Rode (BE). **BUYSENS, Kris, Ph., D.** [BE/BE]; 4 Gentiel Antheunisplein, Bus 12, B-9700 Oudenaarde (BE). **MAETENS, Daniel, Ph., D.** [BE/BE]; Avenue René Comhaire 108, B-1070 Bruxelles (BE).

(74) Agent: **ROELANTS, François**; UCB, S.A., Intellectual Property Dept., Allée de la Recherche 60, B-1070 Bruxelles (BE).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/02504 A1

(54) Title: THERMOSETTING COMPOSITIONS FOR POWDER COATINGS

(57) Abstract: Thermosetting binder compositions for powder coatings comprising a linear or branched carboxylic acid group containing isophtalic acid rich polyester, a linear or branched hydroxyl group containing polyester and a curing agent system having functional groups reactive with the polyester carboxylic acid groups and the hydroxyl groups, wherein the carboxylic group containing isophtalic acid rich polyester is amorphous and the hydroxyl group containing polyester is semicrystalline.

ATTACHMENT F

THERMOSETTING COMPOSITIONS FOR POWDER COATINGS

The present invention relates to thermosetting powder compositions comprising as binder a mixture of carboxyl-terminated polyester, a hydroxyl-terminated polyester, a curing agent system capable of reacting with the carboxylic groups and the hydroxyl groups of the polyesters, and more particularly to thermosetting powder compositions which give coatings having remarkable weatherability, excellent mechanical properties and an outstanding flow.

The invention also relates to the use of said compositions for the preparation of powdered paints and varnishes.

Thermosetting powder compositions are well known in the art and are widely used as paints and varnishes for coating the most various articles. The advantages of these powder coatings are numerous; on the one hand, the problems associated with solvents are completely eliminated, and on the other hand, the powders are used without any loss since only the powder in direct contant with the substrate is retained on the article, the excess powder being, in principle, entirely recoverable and reusable. For these and other reasons, the powder coating compositions are preferred to coating compositions in the form of solutions in organic solvents.

Thermosetting powder compositions have already been widely used in the coating of domestic electrical appliances, automobile industry accessories, and the like. They generally contain a thermosetting organic binder, fillers, pigments, catalysts and various additives used to adapt their properties to their intended use.

There are various types of thermosetting powder compositions. The best known compositions contain as binder either a mixture of carboxyl group-containing polymers, such as a carboxyl group-containing polyester or polyacrylate, and epoxy compounds, such as triglycidyl isocyanurate, glycidyl group-containing acrylic copolymers or β-hydroxyalkylamides or a mixture of hydroxyl group-containing polymers, most often a hydroxyl group-containing polyester, with blocked or non-blockes isocyanates, melamine resins, and the like.

The carboxyl group-containing or the hydroxyl group-containing polyesters suitable for use in the preparation of powdered varnishes and paints have already been described in numerous publications such as articles and patents.

These polyesters are usually prepared from aromatic dicarboxylic acids, mainly terephthalic acid and isophthalic acid and optionally a minor proportion of aliphatic or cycloaliphatic dicarboxylic acids, and from various polyols such as ethyleneglycol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane, and the like.

ATTACHMENT A

These polyesters based on aromatic dicarboxylic acids, when they are used with an appropriate crosslinking agent, provide thermosetting compositions compositions giving paint and varnish coatings possessing good properties, both as regards their appearance and as regards their mechanical properties (impact resistance, flexiblity).

Some of these polyesters and the powders derived from them often are used because of their remarkable weatherability characteristics. These polyesters mostly are derived from isophtalic acid, being the most important acid constituent among others. Yet, the coatings obtained from these polyesters, though proving outstanding weatherability, do not have any flexibility at all.

Currently, the great majority of polyesters used in heat-curable powder compositions are amorphous polyesters. Now, when the polyester is amorphous, it is difficult to prepare perfect heat-curable pulverulent compositions because they have to meet often contradictory criteria. Thus, these powders must not reagglomerate during handling, their transportation and their storage, which implies that the amorphous polyester must possess a sufficiently high glass transition temperature (Tg). On the other hand, in order for the powder particles to be able to coalesce and to form a perfectly homogeneous and uniform coating, it is necessary that the glass transition temperature (Tg) of the polyester is sufficiently low to ensure a low viscosity in the molten state which, itself, ensures good wetting of the pigments and other solid materials accompanying the polyester in the formulation of the said heat-curable powder compositions.

Moreover, the powder must be capable of melting at the stoving temperature in order to form an even film before the crosslinking reaction begins which results in the final curing. In order to obtain good spreading of the molten film over the surface of the substrate, it is therefore necessary for the viscosity of the polyester in the molten state to be sufficiently low. In fact, a very high viscosity in the moten state prevents good spreading of the molten film and is reflected by a loss in the evenness and in the gloss of the coating. Finally, the rate of the crosslinking reaction of the composition can only be controlled by varying the amount and/or the nature of the crosslinking agent and of the crosslinking catalyst which is optionally used.

In order to solve these problems, heat-curable powder compositions have more recently been proposed in which the binder is composed of a crystalline polyester containing carboxyl groups or hydroxyl groups. In fact, the properties of crystalline polyesters make it possible to overcome, to a large extend, the disadvantages

described above which are brought about by the adjustment of the glass transition temperature (Tg), of the viscosity in the molten state and of the reactivity of the amorphous polyesters.

Crystalline polyesters have a melting point greater than 40°C, and, if appropriate, a low glass transition temperature (Tg). This has the consequence that the viscosity in the molten state of crystalline polyesters is much less than that of amorphous polyesters of comparable molecular weight commonly used in heat-curable powder compositions.

This means that powder coating compositions based on crystalline polyesters exhibit a better fluidity of the coating film in the molten state, which gives heat-cured coatings exhibiting an improved appearance.

In addition, by virtue of the crystallinity of the polyesters, the powders formulated with an appropriate crosslinking agent exhibit very good stability towards intermediate storage.

Finally, compared with amorphous polyesters, crystalline polyesters provide coatings having better mechanical properties, in particular excellent flexibility.

The use of semi-crystalline carboxylic acid- or hydroxyl functional polyesters as co-reactable part of the carboxylic acid- or hydroxyl functional amorphous resin respectively, in a binder system along with a hardener being capable of reacting with the resin functional groups, has been subject of several publications in the form of papers and patents such as US 4,859,760, WO 89/05320, WO 94/02552, WO 95/01407, WO 91/14745, WO 97/20895, etc.

Nevertheless, when isophthalic acid rich amorphous polyesters are involved, being especially designed for those applications, where an outstanding weatherability is needed, conflichting properties are observed when hydroxyl group containing or carboxyl group containing resin blends respectively, are compared. So, when a binder composed of a carboxylic acid group containing isophthalic acid rich amorphous polyester along with a carboxylic acid group containing semi-crystalline polyester and a crosslinker having functional groups being reactive with the polyester functional groups, is concerned, the presence of the semi-crystalline polyester induces a huge improvement when flexibility is considered, yet without having a substantial influence on flow.

On the contrary, when a binder composed of a hydroxyl group containing isophthalic acid rich amorphous polyester along with a hydroxyl group containing semi-crystalline polyester and a crosslinker having functional groups being reactive with the polyester functional groups, is concerned, the presence of the semi-

crystalline polyester induces an improved flow along with a moderate influence on flexibility.

In conclusion it can be seen that the various powdered compositions which have been proposed today for outdoor applications all are characterised by one or more disadvantages questioning their suitability.

There is, thus, still a need for powdered thermosetting compositions capable of producing coatings showing an outstanding weatherability and not exhibiting the defects of prior art.

According to the present invention, we have, surprisingly, found that by using as a binder a mixture of a carboxylic acid group containing isophthalic acid rich amorphous polyester along with a hydroxyl group containing semi-crystalline polyester and a curing agent system composed of one curing agent having functional groups being reactive with the amorphous polyester carboxylic acid groups and a second curing agent having functional groups being reactive with the semi-crystalline polyester hydroxyl groups, it is possible to obtain powdered thermosetting compositions which produce coatings proving an outstanding weatherability combined with an excellent flow and flexibility.

Powder coatings having as binder a blend of a carboxylic acid functionalised polyester and an hydroxyl functionalised polyester along with a combination of curing agents having functional groups reactive with the polyester functional groups already have been the object of a few number of patent applications.

JP10017794 (Nippon Ester Co Ltd) describes a polyester resin composition for powder paints containing an acid functionalised polyester having an acid number of at least 40 mg KOH/g, an hydroxyl functionalised polyester having an hydroxyl number situated between 10 and 60 mg KOH/g, an hydroxyalkylamide-based curing agent reactive with the acid functionalised polyester and an isocyanate-based curing agent reactive with the hydroxyl functionalised polyester resin. The particular thermosetting polyester blend of said invention is composed of :

a) 10 to 70 and preferably 20 to 40 parts of the acid functionalised polyester
b) 90 to 30 and preferably 80 to 60 parts of the hydroxyl functionalised polyester

The powder compositions obtained, provide matt or semi-matt coatings with an excellent smoothness and strength.

JP53058536 (Dainippon Ink & Chem.) describes a polyester resin composition for powder paints comprising :

a) 0.5 – 30.0% weight of an carboxylic acid functionalised polyester with an acid number ranging from 30 to 300 mg KOH/g

b) 5 – 59% weight of an hydroxyl functionalised polyester with an hydroxyl number from 10 to 100 mg KOH/g

c) 0.5 - 20.0% of an epoxy resin

d) 3 – 40% weight of a blocked isocyanate

The powder compositions thus obtained, have good edge part properties.

The compositions such as claimed in each of these two patents, do contrast with the composition of the present invention in that the hydroxyl functionalised polyester is not semi-crystalline. Nor are any of the paint performances suggested such as pursued and obtained in the present invention. Besides, nowhere is it stated that the carboxyl functionalised polyesters are preferably used in an excess to the hydroxyl functionalised polyester.

Thus, according to the present invention, there are provided new powdered thermosetting compositions comprising as binder a mixture of a linear or branched carboxylic acid group containing isophtalic acid rich polyester, a linear or branched hydroxyl group containing polyester and a curing agent system having functional groups reactive with the polyester carboxylic acid groups and the hydroxyl groups, wherein the carboxylic group containing isophtalic acid rich polyester is amorphous and the hydroxyl group containing polyester is semi-crystalline.

According to the invention, the curing agent system is preferably composed of at least one curing agent having functional groups reactive with the polyester carboxylic acid groups and at least one curing agent having functional groups reactive with the polyester hydroxyl groups, and/or at least one curing agent having functional groups reactive with both the polyester carboxylic acid groups and the polyester hydroxyl groups.

According to the invention, the carboxylic acid group containing amorphous polyester is preferably composed of a dicarboxylic acid component comprising 50 to 100 mol percentage of isophthalic acid and from 0 to 50 mol percentage of another diacid selected from fumaric acid, maleic acid, phthalic anhydride, isophtalic acid, terephthalic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, succinic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azealic acid, sebacic acid, 1,12-dodecanedioic acid, etc., or the corresponding anhydrides., and of a glycol component comprising 70 to 100 mol percentage of neopentyl glycol and/or 2-butyl- 2-ethyl - 1,3-propanediol and 0 to 30 mol percentage of another glycol selected from ethyleneglycol,

propyleneglycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 2-methyl 1,3-propanediol, hydrogenated Bisphenol A, hydroxypivalate of neopentyl glycol, etc.

According to the invention, the carboxylic acid group containing amorphous polyester can also be a branched polyester incorporating up to 15 mol percentage relative to isophthalic acid, of a polyacid such as trimellitic acid, pyromellitic acid, etc, or their corresponding anhydrides.

In another specific embodiment, the carboxylic acid group containing amorphous polyester may be a branched polyester incorporating up to 15 mol percentage relative to neopentyl glycol and/or 2-butyl-2-ethyl-1,3-propanediol, of a polyol such as trimethylolpropane, ditrimethylolpropane, pentaerythrytol etc.

According to the invention, the hydroxyl functionalised semi-crystalline polyester is preferably composed of 75 - 100 mol percentage of terephthalic acid and/or 1,4-cyclohexanedicarboxylic acid and from 0 to 25 mol percentage of another diacid selected from fumaric acid, maleic acid, phthalic anhydride, isophthalic acid, terephthalic acid, 1,4 cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, succinic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azealic acid, sebacic acid, 1,12-dodecanedioic acid, etc., and of a glycol component comprising from 75 to 100 mol percentage of an aliphatic non-branched diol selected from ethyleneglycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol 1,9-nonanediol, 1,10-decanediol, 14-tetradecanediol, 1,16-hexadecanediol, etc. used in a mixture or alone, and 0 to 25 mol percentage of another glycol selected from propyleneglycol, neopentyl glycol, 2-methyl-1,3-propanediol, 2-butyl,2-ethyl-1,3-propanediol, hydrogenated Bisphenol A, hydroxypivalate of neopentyl glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, etc.

According to the invention, the hydroxyl functionalised semi-crystalline polyester may also be composed of 75 - 100 mol percentage of a linear non branched aliphatic diacid selected from succinic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azealic acid, sebacic acid, 1,12-dodecanedioic acid, etc. used in a mixture or alone, and from 0 to 25 mol percentage of another diacid selected from fumaric acid, maleic acid, phthalic anhydride, terephthalic acid, isophthalic acid, 1,2 cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, etc., and of a glycol component comprising from 75 to 100 mol percentage of a cycloaliphatic diol such as 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, hydrogenated Bisphenol A, etc. used in a mixture or

alone, or an aliphatic non-branched diol such as ethyleneglycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6 hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 14 tetradecanediol, 1,16-hexadecanediol, etc. used in a mixture or alone, and from 0 to 25 mol percentage of another glycol selected from propyleneglycol, neopentyl glycol, 2-methyl-1,3-propanediol, 2-butyl, 2-ethyl-1,3-propanediol, 1,4-cyclohexanediol, 1,4 cyclohexanedimethanol, hydrogenated Bisphenol A, etc.

In a specific embodiment, the hydroxyl functionalised semi-crystalline polyester of the binder may be a branched polyester incorporating up to 15 mol percentage based on the total of terephthalic acid, 1,4-cyclohexanedicarboxylic acid or non-branched aliphatic diacids, of a polyacid such as trimellitic asid, pyromellitic acid, etc., or their corresponding anhydrides.

In another specific embodiment, the hydroxyl functionalised semi-crystalline polyester may be a branched polyester incorporating up to 15 mol percentage based on the total of aliphatic non-branched diols or cycloaliphatic diols, of a polyol such as trimethylolpropane, ditrimethylolpropane, pentaerythrytol etc.

The hydroxyl functionalised semi-crystalline polyester may also be a branched polyester incorporating up to 30 mol percentage based on the total of terephthalic acid, 1,4-cyclohexanedicarboxylic acid or non-branched aliphatic diacids and/or on the total of aliphatic non-branched diols or cycloaliphatic diols, of monofunctional carboxylic acids having at least two hydroxyl groups wherein one or more of the hydroxyl groups can be hydroxyalkyl substituted, selected from α,α-bis-(hydroxymethyl)-propionic acid (dimethylolpropionic acid), α,α-bis-(hydroxymethyl)-butyric acid, α,α,α,-tris(bydroxymethyl)-acetic acid, α,α-bis-(hydroxymethyl)-valeric acid, α,α-bis-(hydroxy) propionic acid or α-phenylcarboxylic acids having at least two hydroxyl groups directly pandant to the phenyl ring (phenolic hydroxyl groups) such as 3,5-dihydroxybenzoic acid, etc.

According to the present invention, the carboxylic acid group containing isophthalic acid rich polyester in the binder very suitably has:

- an acid number from 15 to 100 mg KOH/g and preferably from 30 to 70 mg KOH/g;
- a number averaged molecular weight ranging from 1100 to 15000 and preferably from 1600 to 8500, measured by gel permeation chromatography (GPC);

- a glass transition temperature (Tg) from 40 to 80°C, measured by Differential Scanning Calorimetry according to ASTM D3418 with a heating gradient of 20°C per minute ; and
- an ICI (cone/plate) viscosity at 200°C ranging from 5 to 15000 mPa.s accordingly to ASTM D4287-88

According to the present invention, the hydroxyl group containing semi-crystalline in the binder very suitably has:

- an hydroxyl number from 10 to 100 mg KOH/g and preferably from 15 to 80 mg KOH/g;
- a number averaged molecular weight ranging from 1100 to 17000 and preferably from 1400 to 11200;
- a fusion zone from 50 to 150°C, measured by Differential Scanning Calorimetry (DSC) according to ASTM D3418 with a heating gradient of 20°C per minute;
- a glass transition temperature (Tg) from -50 to 50°C, measured by Differential Scanning Calorimetry according to ASTM D3418 with a heating gradient of 20°C per minute;
- a degree of crystallinity of at least 5 J/g and preferably 10J/g, measured by Differential Scanning Calorimetry according to ASTM D3415 with a heating gradient of 20°C per minute; and
- an ICI (cone/plate) viscosity measured by Differential Scanning Calorimetry according to ASTM D4287-88, measured 175°C ranging from 5 to 10000 mPa.s

In a specific embodiment, the thermosetting polyester blend of the binder is composed of :

- 55 to 95 and preferably 70 to 90 parts by weight of the carboxylic acid group containing isophthalic acid rich amorphous polyester; and
- 45 to 5 and preferably 30 to 10 parts by weight of the hydroxyl group containing semi-crystalline polyester.

The particular thermosetting polyester blend can be obtained by dry blending the amorphous and the semi-crystalline polyester using a mechanical mixing procedure as available for the premixing of the powder paint constituents.

Alternatively the amorphous and the semi-crystalline polyester can be blended in the melt using the conventional cylindrical double-walled reactor or by extrusion such as the Betol BTS40.

According to the present invention, the curing agent having functional groups reactive with the carboxylic acid groups of the isophthalic acid rich amorphous

polyester is, more in particular, a polyepoxy compound or a β-hydroxyalkylamide containing compound.

Among the curing agents having functional groups reactive with the carboxylic acid groups of the amorphous polyester, following compounds may be used :

- polyepoxy compounds solid at room temperature and containing at least two epoxy groups per molecule such as, for example, triglycidyl isocyanurate like the one marketed under the name Araldite PT810 (Ciba) or the epoxy resin Araldite PT910 (Ciba)
- β-hydroxyalkylamides which contain at least one, preferably two bis(β-hydroxyalkyl)amide groups, for example, those mentioned in International patent application US-A-4727111, US-A-4788255, US-A-4076917, EP-A-322834 and EP-A-473380.
- Acrylic copolymers containing glycidyl groups obtained from glycidyl methacrylate and/or glycidyl acrylate and a (meth)acrylic monomer and, optionally, an ethylenically mono-unsaturated monomer different from glycidyl (meth)acrylate or from the (meth)acrylic monomer. An example of this type of acrylic copolymer is GMA252 marketed by Estron Chemical Inc, and is mentioned in International patent application PCT WO91/01748.

The curing agent described herein above is used in an amount from 0.25 to 1.40 preferably from 0.60 to 1.05 equivalent of carboxyl group present in the amorphous polyester per equivalent of epoxy or β-hydroxyalkyl groups.

Also according to the present invention, the curing agent having functional groups reactive with the hydroxyl groups of the semi-crystalline polyester, may be a blocked polyisocyanate compound.

Among the curing agents having functional groups reactive with the hydroxyl groups of the semi-crystalline polyester, the suitable blocked isocyanate crosslinking agents, well known in the art, may be used.

Examples of the blocked polyisocyanate crosslinking compounds include those which are based on isophorone diisocyanate blocked with ε-caprolactam, commercially available as Hüls B1530, Ruco NI-2 and Cargill 2400, or toluene-2,4-diisocyanate blocked with ε-caprolactam, commercially available as Cargill 2450, and phenol-blocked hexamethylene diisocyanate.

Another class of blocked polyisocyanate compounds which may be employed are adducts fo the 1,-diazetidine-2,4-dione dimer of isophorone diisocyanate and a diol, wherein the ratio of NCO to OH-groups in the formation of the adduct is about 1:0.5 to 1:0.9, the mole ratio of diazetidinedione to diol is from 2:1 to 6:5, the

content of free isocyanate groups in the adduct is not greater than 8 weight percent and the adduct has a molecular weight of about 500 to 4000 and a melting point of about 70 to 130°C. Such an adduct is commercially available under the name Hüls BF1540.

The crosslinking agent described herein above is used in an amount from 0.3 to 1.4 preferably from 0.7 to 1.2 equivalent of hydroxyl group present in the semi-crystalline polyester per equivalent of isocyanate.

The carboxylic acid group containing amorphous polyester and the hydroxyl group containing semi-crystalline polyester, according to the present invention, are prepared using conventional esterification techniques well known in the art. The polyesters are prepared according to a procedure consisting of one or more reaction steps.

For the preparation of these polyesters, a conventional reactor equipped with a stirrer, an inert gas (nitrogen) inlet, a thermocouple, a distillation column connected to a water-cooled condenser, a water separator and a vacuum connection tube is used.

The esterification conditions used to prepare the polyesters are conventional, namely a standard esterification catalyst, such as dibutyltin oxide, dibutyltin dilaurate, n-butyltin trioctoate, sulphuric acid or sulphonic acid, can be used in an amount from 0.05 to 1.50% by weight of the reactants and optionally, colour stabilisers, for example, phenolic antioxidants such as Irganox 1010 (Ciba) or phosphonite- and phosphite-type stabilisers such as tributylphosphite, can be added in an amount from 0 to 1% by weight of the reactants.

Polyesterification is generally carried out at a temperature which is gradually increased from 130°C to about 190 to 250°C, first under normal pressure, then, when necessary, under reduced pressure at the end of each process step, while maintining these operating conditions until a polyester is obtained, which has the desired hydroxyl and/or acid number. The degree of esterification is followed by determining the amount of water formed in the course of the reaction and the properties of the obtained polyester, for example the hydroxyl number, the acid number, the molecular weight or the viscosity.

When polyesterification is complete, crosslinking catalysts can optionally be added to the polyesters while they are still in the molten state. These catalysts are added in order to accelerate crosslinking of the thermosetting powder composition during curing and further called accelerators for that reason. Examples of such accelerators include amines (e.g. 2-phenylimidazoline), phosphines (e.g.

triphenylphosphine), ammonium salts (e g. tetrabutylammonium bromide or tetrapropylammoium chloride), phosphonium salts (e.g. ethyltriphenylphosphonium bromide or tetrapropylphosphonium chloride) and organo-tin compounds (e.g. dibutyltin dilaurate, dibutyltin dimaleate, dibutyltin oxide, stannous octoate, 1,3-diacetoxy-1,1,3,3-tetrabutyldistanoxane). These accelerators are preferably used in an amount of 0 to 5% with respect of the weight of the polyester.

In a specific embodiment, the binder may substantially be based on:

- 28 to 93, preferably 43 to 86 parts by weight of the carboxylic acid group containing isophthalic acid rich amorphous polyester
- 43 to 3, preferably 29 to 7 parts by weight of the hydroxyl group containing semi-crystalline polyester
- 1 to 45, preferably 3 to 35 parts by weight of a curing agent having functional groups being reactive with the carboxylic acid groups of the amorphous polyester
- 21.0 to 0.1, preferably 9.0 to 0.5 parts by weight of a curing agent having functional groups reactive with the hydroxyl groups of the semi-crystalline polyester

based on the total weight of polyester resins and curing agents.

In addition to the essential components described above, compositions within the scope of the present invention can also include flow control agents such as Resiflow PV5 (Worlee), Modaflow (Monsanto) Acronal 4F (BASF), etc., and degassing agents such as benzoin (BASF) etc. To the formulation UV-light absorbers such as Tinuvin 900 (Ciba), hindered amine light stabilisers represented by Tinuvin 144 (Ciba), other stabilizing agents such as Tinuvin 312 and 1130 (Ciba), antioxidants such as Irganox 1010 (Ciba) and stabilisers from the phosphonite or phosphite type can be added.

Both, pigmented systems as well as clear lacquers can be prepared.

A variety of dyes, pigments and fillers can be utilised in the composition of this invention. Examples of useful pigments and dyes are: metallic oxides such as titaniumdioxide, ironoxide, zincoxide and the like, metal hydroxides, metal powders, sulphides, sulfates, carbonates, silicates such as ammoniumsilicate, carbon black, talc, china clay, barytes, iron blues, leadblues, organic reds, organic maroons and the like.

The components of the composition according to the invention may be used as the coating material for entirely or partially coated substrate. For that purpose, the

components may be mixed by dry blending in a mixer or blender (e.g. drum mixer). The premix is then homogenised at temperatures ranging from 70 to 150°C in a single screw extruder such as the BUSS-Ko-Kneter or a double screw extruder such as the PRISM or APV. The extrudate, when cooled down, is grounded to a powder with a particle size ranging from 10 to 150 µm. The powdered composition may be deposed on the substrate by use of a powder gun such as an electrostatic CORONA gun or TRIBO gun. On the other hand well known methods of powder deposition such as the fluidised bed technique can be used. After deposition the powder is heated to a temperature between 160 and 220°C, causing the particles to flow and fuse together to form a smooth, uniform, continuous, uncratered coating on the substrate surface.

The following examples are submitted for a better understanding of the invention without being restricted thereto.

Example 1: Synthesis of an isophthalic acid rich polyester

A mixture of 398.6 parts of neopentyl glycol and 22.2 parts of trimethylpropane is placed in a conventional four neck round bottom flask equipped with a stirrer, a distillation column connected to a water cooled condenser, an inlet for nitrogen and thermometer attached to a thermoregulator.

The flask contents are heated, while stirring under nitrogen, to a temperature of circa 130°C at which point 721.1 parts of isophthalic acid and 2.5 parts of n-butyltintrioctoate are added. The heating is continued gradually to a temperature of 230°C. Water is distilled from the reactor from 180°C on. When distillation under atmospheric pressure stops, a vacuum of 50 mm Hg is gradually applied. After three hours at 230°C and 50 mm Hg, following characteristics are obtained:

AN	32 mg KOH/g
OHN	2 mg KOH/g
ICI $^{200°C}$ (cone/plate)	8000 mPa.s
Tg (DSC, 20°/min)	59°C

The carboxyl functionalised polyester is cooled down to 180°C and 2.5 parts of tri(2,4-di-tert.-butylphenyl)phosphite and 2.5 parts of octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)propionate are added. After half an hour of stirring the reactor is discharged.

Example 2:

According to the procedure described in the Example 1, 429.3 parts of neopentyl glycol and 714.3 parts of isophthalic acid are put into reaction until a polyester with following characteristics is obtained:

AN	21 mg KOH/g
OHN	3 mg KOH/g
ICI $^{200°C}$ (cone/plate)	5200 mPa.s
Tg (DSC, 20°/min)	63°C

To the polyester standing at 180°C tri(2,4-di-tert.-butylphenyl)phosphite and octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)propionate are added. After one hour of stirring the reactor is discharged.

Example 3:

A mixture of 400.7 parts of neopentyl glycol and 14.5 parts of trimethylolpropane is placed in a reactor as for Example 1. At a temperature of 130°C 186.7 parts of terephthalic acid, 435.6 parts of isophthalic acid and 2.5 parts of n-butyltintrioctoate are added. The reaction is continued at 220°C under atmosphric pressure until about 95% of the theoretical amount of water is distilled and a transparent hydroxyl functionalised prepolymer with the following characteristics is obtained:

AN	8 mg KOH/g
OHN	47 mg KOH/g

To the first step prepolymer standing at 200°C, 98.0 parts of isophthalic acid are added. Thereupon, the mixture is gradually heated to 230°C. After a 2 hour period at 230°C and when the reaction mixture is transparent, a vacuum of 50 mm Hg is gradually applied. After 3 hours at 230°C and 50 mm Hg, following characteristics are obtained:

AN	32.6 mg KOH/g
OHN	3 mg KOH/g
ICI $^{200°C}$ (cone/plate)	5600 mPa.s
Tg (DSC, 20°/min)	61°C

To the polyester standing at 180°C tri(2,4-di-tert.-butylphenyl)phosphite and octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)propionate are added. After half an hour of stirring the reactor is discharged.

Example 4:

According to the procedure described in Example 3, 368.3 parts of neopentyl glycol, 39.8 parts of trimethylolpropane, 367.4 parts of terephthalic acid and 193.5 parts of isophthalic acid are put into reaction until a hydroxyl funtionalised prepolymer with following characteristics are obtained:

AN	5 mg KOH/g
OHN	83 mg KOH/g

To the hydroxyl functionalised prepolymer 174.4 parts of isophthalic acid are added and the reaction is continued as in Example 3 until following characteristics are obtained:

AN	50.8 mg KOH/g
OHN	1.1 mg KOH/g
ICI $^{200°C}$ (cone/plate)	7100 mPa.s

To the polyester standing at 180°C tri(2,4-di-tert.-butylphenyl)phosphite and octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)propionate are added. After half an hour of stirring the reactor is discharged.

Example 5 (comparative example):

According to the procedure described in Example 1, 434.7 parts of neopentyl glycol, 22.2 parts of trimethylolpropane and 690.4 parts of isophthalic acid are put into reaction until a hydroxyl functionalised polyester with following characteristics is obtained:

AN	3 mg KOH/g
OHN	31.5 mg KOH/g
ICI $^{200°C}$ (cone/plate)	4700 mPa.s
Tg (DSC, 20°/min)	57°C

Example 6:

A mixture of 544.5 parts of 1,4-cyclohexanedimethanol, 39.9 parts of trimethylolpropane, 551.8 parts of adipic acid and 2.5 parst of n-butyltintrioctoate

is placed in a reactor as for Example 1. The flask contents are heated, while stirring under nitrogen to a temperature of circa 140°C, at which point water is distilled from the reactor. The heating is continued gradually to a temperature of 220°C. When distillation under atmospheric pressure stops, 1.0 part of tributylphophite and 1.0 part of n-butyltintrioctoate are added and a vacuum of 50 mm Hg is gradually applied. After 5 hours at 220 °C and 50 mm Hg, the following characteristics are obtained:

AN	3 mg KOH/g
OHN	53 mg KOH/g
ICI $^{125°C}$ (cone/plate)	2800 mPa.s
ICI $^{100°C}$ (cone/plate)	6800 mPa.s
Fusion zone	70 - 88°C

The hydroxyl functionalised polyester is cooled down to 160°C and 5 parts of Tinuvin 144, 10 parts of Tinuvin 1130 and 10 parts of Tinuvin 312 are added. After one hour stirring the resin is discharged.

Example 7:

According to the procedure described in Example 6, 521.1 parts of 1,4-cyclohexanedimethanol, 22.5 parts of trimethylolpropane and 528.1 parts of adipic acid are put into reaction until a hydroxyl functionalised prepolymer with following characteristics is obtained:

AN	3 mg KOH/g
OHN	32 mg KOH/g

To the hydroxyl functionalised prepolymer standing at 175°C, 67.5 parts of 2,2-bis(hydroxymethyl)propionic acid are added. The temperature is increased to 220°C and a vacuum of 50 mm Hg is gradually applied until a hydroxyl functionalised resin with following characteristics is obtained:

AN	6 mg KOH/g
OHN	62 mg KOH/g
ICI $^{150°C}$ (cone/plate)	4100 mPa.s
Fusion zone	65 - 78°C

Example 8:

According to the procedure described in Example 6, 505.2 parts of 1,4-cyclohexanediol, 16.0 parts of trimethylolpropane and 635.6 parts of adipic acid are put into reaction until a resin with following characteristics is obtained:

AN	3 mg KOH/g
OHN	19 mg KOH/g
ICI $^{175°C}$ (cone/plate)	4900 mPa.s
ICI $^{200°C}$ (cone/plate)	2400 mPa.s
Fusion zone	78- 114°C

Example 9:

According to the procedure described in Example 7, 222.9 parts of ethyleneglycol and 790.4 parts of dodecanoic acid are put into reaction until a hydroxyl functionalised prepolymer with following characteristics is obtained:

AN	3 mg KOH/g
OHN	24 mg KOH/g

The hydroxyl functionalised prepolymer standing at 175°C, 42.0 parts of 2,2-bis(hydroxymethyl)propionic acid are added and the reaction is continued as in Example 7, until a hydroxyl functionalised prepolymer with following characteristics is obtained:

AN	4 mg KOH/g
OHN	42 mg KOH/g

The hydroxyl functionalised polyester thus obtained, is cooled down to 175°C and 85.1 parts of 2,2-bis(hydroxymethyl)propionic acid are added. The temperature is increased to 220°C and a vacuum of 50 mm Hg is gradually applied until a hydroxyl functionalised prepolymer with following characteristics is obtained:

AN	8 mg KOH/g
OHN	79 mg KOH/g
ICI $^{150°C}$ (cone/plate)	2000 mPa.s
Fusion zone	71- 89°C

Example 10:

According to the procedure described in Example 6, 492.6 parts of 1,6-hexanediol and 648.0 parts of terephthalic acid are put into reaction until a hydroxyl functionalised resin with following characteristics is obtained:

AN	1 mg KOH/g
OHN	33 mg KOH/g
ICI $^{150°C}$ (cone/plate)	4400 mPa.s
ICI $^{175°C}$ (cone/plate)	2000mPa.s
Fusion zone	133- 144°C

Example 11:

According to the procedure described in Example 6, 556.6 parst of 1,4-cyclohexanedimethanol, 15.9 parts of trimethylolpropane and 564.1 parts of adipic acid are put into reaction until a hydroxyl functionalised resin with following characteristics is obtained:

AN	2 mg KOH/g
OHN	23 mg KOH/g
ICI $^{150°C}$ (cone/plate)	1500 mPa.s
Fusion zone	82- 112°C

Example 12:

According to the procedure described in Example 10, 454.9 parts of 1,6-hexanediol and 591.8 parts of terephthalic acid are put into reaction until a hydroxyl functionalised prepolymer with following characteristics is obtained:

AN	9 mg KOH/g
OHN	49 mg KOH/g

To the hydroxyl functionalised prepolymer, standing at 200°C, 92.0 parts of isophthalic acid are added. The reaction temperature is increased to 230°C and a vacuum of 50 mm Hg is gradually applied until a carboxyl functionalised polyester with following characteristics is obtained:

AN	31 mg KOH/g
OHN	1 mg KOH/g
ICI $^{150°C}$ (cone/plate)	7200 mPa.s
ICI $^{175°C}$ (cone/plate)	3000 mPa.s
Fusion zone	133- 146°C

Example 13 (comparative example):

According to the procedure described in Example 6, 530.8 parts of 1,4-cyclohexanedimethanol, 15.9 parts of trimethylolpropane and 589.9 parts of adipic acid are put into reaction until a carboxyl functionalised polyester with following characteristics is obtained:

AN	21 mg KOH/g
OHN	3 mg KOH/g
ICI $^{200°C}$ (cone/plate)	6400 mPa.s
Fusion zone	100- 130°C

Example 14: Synthesis of an accelerator containing masterbatch

For the thermosetting reaction between the hydroxyl functions of the hydroxyl functionalised semi-crystalline polyester and the reactive groups of the appropriate crosslinker, an organo-tin compound such as dibutyltindilaurate is added as accelerator. For feasability reasons, the accelerator, being a liquid, is added to the premix as a masterbatch.

According to the procedure of Example 1, 397.0 parts of neopentyl glycol, 13.4 parts trimethylolpropane and 631.3 parts of isophthalic acid are put into reaction until a polyester with following characteristics is obtained:

AN	2 mg KOH/g
OHN	21 mg KOH/g
ICI $^{200°C}$ (cone/plate)	12500 mPa.s
Tg (DSC, 20°/min)	60°C

To the hydroxyl functionalised polyester standing at 180°C, 50.0 parts of dibutyltindilaurate are added. After half an hour of stirring the resin is discharged.

Example 15:

The polyester as illustrated above, are then formulated to a powder accordingly to one of the formulations as mentionned below.

Formulation A White paint formulation		Formulation B Brown paint formulation		Formulation C Green paint formulation	
Binder	69.06	Binder	78.33	Binder	
Kronos 2310	29.60	Bayferrox 130	4.44	66.10	
Resiflow PV5	0.99	Bayferrox 3950	13.80	Kronos 2310	3.95
Benzoin	0.35	Carbon Black FW2	1.09	Sicomin L1522	23.67
		Resiflow PV5	0.99	Heliogene Blue K7090	0.99
		Benzoin	0.35	Carbon Black 101	3.95
				Resiflow PV5	0.99
				Benzoin	
				0.35	

For the preparation of the powder formulation, the carboxyl functionalised isophthalic acid rich amorphous polyester resin and the hydroxyl functionalised semi-crystalline polyester resin can be used as a blend or as separate resins. When used as a blend, blending is done by mixing the respectively resins in the molten state using a conventional round bottom flask.

The powders are prepared first by dry blending of the different components and then by homogenisation in the melt using a PRISM 16 mm L/D 15/1 twin screw extruder at an extrusion temperature of 85°C. The homogenised mix is then cooled and grinded in a Alpine 100 UPZII. Subsequently the powder is sieved to obtain a particle size between 10 and 110 µm. The powder thus obtained is deposited on chromated (Cr^{6+}) aluminium H5005, DIN 50939 with a thickness of 1 mm, by electrostatic deposition using the GEMA – Volstatic PCG 1 spraygun. At a film thickness between 50 and 80 µm the panels are transferred to an air-ventilated oven, where curing proceeds for 15 minutes at a temperature of 200°C. The paint characteristics for the finished coatings obtained from the combination of the different amorphous and semi-crystalline polyesters, as illustrated in this invention, are reproduced in the tables below. In the same tables are reproduced, as comparative examples, the paint performances of the powders derived from a blend of a carboxyl functionalised amorphous and a carboxyl functionalised semi-crystalline polyester (example 25 & 29) on the one hand and from a blend of a hydroxyl functionalised amorphous and a hydroxyl functionalised semi-crystalline

polyester (example 26 & 28) on the other hand. Example 25 & 29 thus answers a composition as claimed in PCT WO91/14745 (Courtaulds Coatings Ltd), meanwhile Example 26 and 28 complies with those compositions such as described in PCT WO89/05320 (Eastman Kodak).

Table 1

Example	Formulation	Resin X/Y	Resin X	Resin Y	Curing Agent X	Curing Agent Y	Accelerator
16	A	80/20	1 = 49.23	6 = 12.31	pT810 = 3.71	LS2147 = 2.34	1.48
17	A	75/25	1 = 46.07	7 = 15.36	XL552 = 2.42	LS2147 = 3.37	1.84
18	A	85/15	4 =52.16	8 = 9.21	PT810 = 5.80	BF1540 = 0.80	1.10
19	A	80/20	2 = 49.91	9 = 12.48	XL552 = 1.86	LS2147 = 3.32	1.50
20	A	70/30	3 = 35.29	6 = 15.13	GMA252 = 13.05	B1530 = 3.78	1.82
21	A	85/15	3 = 52.12	6 = 9.20	PT910 = 5.15	LS2147 = 1.50	1.10
22	B	75/25	1 = 46.66	6 = 15.55	XL552 = 2.46	LS2147 = 2.53	1.87
23	B	80/20	3 = 48.55	9 = 12.14	PT810 = 3.65	BF1540 = 3.27	1.46
24	C	75/25	2 = 47.29	10 = 15.76	PT810 = 1.97	BF1540 = 2.15	1.9
25	A	80/20	1 = 51.38	12 = 12.85	PT810 = 4.83	/	/
26	A	80/20	5 = 43.98	10 = 10.99	/	BF1540 = 7.50	6.60
27	A	80/20	1 = 51.41	11 = 12.85	PT810 = 2.14	B1530 = 1.12	1.54
28	A	80/20	5 = 44.33	11 = 11.08	/	B1530 = 7.01	6.65
29	A	80/20	1 = 51.71	13 = 12.93	PT810 = 4.43	/	/
30	A	80/20	5 = 47.07	13 = 11.77	B1530 = 4.09	PT810 = 0.49	5.65

Table 1 indicates the powder compositions according to the invention (example 16 to 24 and example 27) as well as the powder compositions according to prior art such as Courtaulds Coatings (example 25 and 29) and Eastman Kodak (example 26 and 28) respectively. The powder composition of example 30 is given as comparative example in which the amorphous isophthalic acid rich polyester is hydroxyl functionalised, meanwhile the semi-crystalline polyester is carboxyl functionalised. In this table:

Column 1: indicates the identification number of the formulation

Column 2: indicates the type of formulation

A = white (RAL9010)

B= medium brown (RAL8014)

C= Dark Green (RAL6005)

Column 3: indicates the weight ratio of the amorphous over the semi-crystalline polyester

Column 4: indicates the type (example) and quantity of the amorphous polyester used in the formulation

Column 5: indicates the type (example) and quantity of the semi-crystalline polyester used in the formulation

Column 6: indicates the type and quantity of the curing agent having functional groups being reactive with the polyester carboxylic groups where:

PT810 = Araldite 810 (Ciba) = triglycidylisocyanurate

PT910 = Araldite 910 (Ciba) = diglycidylterephthalate/ triglycidyltrimellitate mixture (75/25)

XL552 = Primid XL552 (EMS) = N,N,N',N'-tetrakis-(2-hydroxyethyl)-adipamide

GMA252 (Estron) = glycidyl group containing acrylic copolymer

Column 7: indicates the type and quantity of the curing agent having functional groups being reactive with the polyester hydroxyl groups where:

LS2147 (Bayer) = cycloaliphatic polyuretdione

B1530 (Hüls) = ε-caprolactam blocked isophorone diisocyanate

BF1540 (Hüls) = uretdione blocked isophorone diisocyanate

Column 8: indicates the amount of accelerator containing masterbatch, needed for accelerating the reaction between the hydroxyl functions of the polyester and the isocyanate functions of the curing agent.

In table 2 the paint performances of the powder paints of example 16 to 30, obtained after a 15-minute curing schedule at 200°C, are reproduced.

Table 2

Powder	Gloss 60°	DI	RI	T-bending	Erichsen slow embossing	Pencil hardness	Aspect	Long wave	Short wave
example 16	93	180	160	0T	9.2	2H	g	27.1	26.1
example 17	93	160	160	0T	8.9	H	g	26.0	26.9
example 18	90	160	140	0T	9.0	H	g	27.6	25.3
example 19	94	160	140	0T	8.8	H	g	27.4	26.3
example 20	92	160	140	0T	9.1	F	g	28.1	26.2
example 21	92	120	120	0T	8.7	2H	g	23.4	22.8
example 22	88	160	160	0T	9.3	H	g	24.9	23.2
example 23	90	160	160	0T	9.4	2H	g	25.0	23.7
example 24	94	160	140	0T	9.1	H	g	26.8	25.9
example 25	92	160	160	0T	9.3	H	m - b	65.1	57.3
example 26	90	60	40	> 2T	5.8	H	g	27.3	25.7
example 27	90	200	200	0T	9.0	H	g	25.6	25.4
example 28	89	0	20	> 2T	4.5	H	g	27.4	25.3
example 29	91	160	140	0T	9.4	H	m	53.8	50.5
example 30	88	40	20	> 2T	3.8	H	g	28.0	25.7

In this table:

Column 1: represents the identification of the illustrated example

Column 2: indicates the 60° gloss, measured according to ASTM D523

Column 3: indicates the direct impact strength according to ASTM D2794. The highest impact which does not crack the coating is recorded in kg.cm.

Column 4: indicates the reverse impact strength according to ASTM D2794. The highest impact which does not crack the coating is recorded in kg.cm.

Column 5: indicates the value of T-bend according to ASTM D4145-83. The minimum T-bend to no paint fracture is recorded.

Column 6: indicates the Erichsen slow embossing according to ISO 1520. The highest penetration which does not crack the coating is recorded in mm.

Column 7: indicates the pencil hardness according to the scratch Hardness Tester according to Wolff-Wilborn

Column 8: indicates the aspect of the coating:

g very smooth, mirror-like finish

m: orange peel

b: strong orange peel

Column 9: indicates the "long waviness" as measured with the BYK-Gardner surface tester.

Column 10: indicates the "short waviness" as measured with the BYK-Gardner surface tester.

As appears from the table 2, the powders according to the present invention (example 16 to 24 and example 27) thus prove to satisfy a combination of properties, such as outstanding flexibility and flow, which were never obtained from powder formulations as claimed in prior art. As clearly demonstrated in examples 25 and 29, the combination of an isophthalic acid rich carboxylic acid group containing amorphous polyester and a semi-crystalline carboxylic acid group containing polyester along with an curing agent having functional groups reactive with both the polyesters carboxylic groups, such as claimed in international patent application PCT WO91/14745 (Courtaulds Coatings), results in powder coatings which, upon curing, prove an excellent flexibility, yet without an acceptable aspect paticularly observed as a mediocre to strong orange peel. Otherwise, and as demonstrated in examples 26 and 28, the combination of an isophthalic acid rich hydroxyl group containing amorphous polyester and a semi-crystalline hydroxyl group containing polyetser along with an curing agent having functional groups reactive with both the polyesters hydroxyl groups, such as claimed in international

patent application PCT WO89/05320 (Eastman Kodak), results in powder coatings which, upon curing, prove an outstanding flow, typical of blocked isocyanate based powder coatings, yet without meeting the requirements for impact and T-bending tests.

Similarly, when hydroxyl group containing isophthalic acid rich amorphous polyester is combined with a carboxylic group containing semi-crystalline polyetser along with two curing agents, one of which having functional groups reactive with carboxylic acid functions and the other one having functional groups reactive with hydroxyl functions, the powder derived proves upon curing an outstanding flow, without any flexibility.

The advantageous influence on flow as obtained by curing the powder coating compositions of the present invention, more clearly appears when "wave scan" measurements are considered.

The so-called "wave scan" (BYK-Gardner, Application report wave scan, Germany, 1992) was developed by BYK-Gardner in order to simulate the visual impression obtained from optical inspection of surface structures. Here, the measuring principle is based on modulation of the light from a small diode reflected by the surface structures of the sample. The laser light shines on the surface at an angle of 60°, and the reflected light is detected at the gloss angle (60° opposite). During the measurement, the wave scan is moved across the sample surface over a scan length of about 10 cm, with a data point recorded every 0.08 mm. The measured data of the brightness profile (modulation of the reflected light) are first separated by mathematical filtering into a long wave (structural size > 0.6 mm) and a short wave (structural size < 0.6 mm). The values of so-called "long waviness" (structures from 10 to 0.6 mm) and "short waviness" (structures from 0.6 to 0.1 mm) result from the variance of the filtered data. Here, the measuring scale goes from 0 to 100, with lower values indicating a smoother structure.

Besides an oustanding flexibility and flow, the powder coating compositions of the present invention prove to satisfy an excellent outdoor resistance comparable to or better than the currently used nowadays commercial polyester based powders. For outdoor resistance, accelerated weathering as well as acid hydrolysis are verified. In table 3, the relative gloss values, recorded every 400 hours, according to ASTM D523, are reported for the coating obtained from examples 22 and 23, submitted to the Q-UV accelerated weathering test. In the same table are given the weathering results for the resins of examples 1 and 3, as well as of a commercial carboxylic acid functionalised amorphous polyester (Crylcoat 440 from UCB Chemicals) all

formulated in a 93/7 ratio with PT810 according to the brown paint formulation as in formulation B.

In this table only gloss reductions until 50% of the maximum value are mentionned. Weathering measurement are conducted in a very severe environment, i.e. the Q-UV accelerated weathering tester (Q-Panel Co) according to ASTM G53-88 (standard practice for operating light and water exposure apparatus – fluorescent UV/condensation type - for exposure of non metallic materials).

For this table, coated panels have been subjected to the intermittent effects of condensation (4 hours at 50°C) as well as the damaging effects of sunlight simulated by fluorescent UV-A lamps (340 nm, I = 0.77 W/m²/nm) (8 hours at 60°C). For this type of lamps a good correlation with natural sunlight is observed, contrary to the UV-B 313 nm lamps, where unwanted or unnatural chemical reactions are induced, as described in "Methods for UV Durability Predictions of Polymer Coatings" from Courtaulds Coatings Ltd. as presented during the XXth International Conference in Organic Coatings/Science and Technology (Athens, Greece, 07/94) or as described in the Technical Bulletin L8006 from Q-Panel or by N. Patel, JOCCA 3, 104, (1991).

The panels used in the Q-UV are chromated aluminium ones.

Table 3

UV-A (340 nm, I=0.77 W/m²/nm)					
Hours	Example 22	Formulation B Example 1	Example 23	Formulation B Example 3	Formulation B Crylcoat 440
0	100	100	100	100	100
400	99	100	100	100	99
800	100	99	98	100	96
1200	99	100	97	97	95
1600	99	100	97	97	80
2000	98	100	95	97	74
2400	99	98	93	96	42
2800	99	99	89	95	
3200	98	98	83	92	
3600	99	96	76	89	
4000	97	91	68	87	
4400	97	89	61	84	
4800	96	86	56	78	
5200	93	80	48	68	
5600	87	76		63	
6000	84	74		54	
6400	73	60		45	
6800	64	54			
7200	58	48			
7600	55				
8000	52				
8400	46				

In table 4, the acid hydrolysis resistance of the coating of example 24 as well as of a commercial carboxylic acid functionalised amorphous polyester (Crylcoat 440 from UCB Chemicals) formulated in a 93/7 ratio with PT810 according to the green paint formulation as in formulation C, is reproduced by indicating the Δb^* -values according to "Compagnie Internationale d'Eclarage" L*a*b* - colour measurement method (CIE – L*a*b*).

Acid hydrolysis resistance is determined according to ISO3231 (Determination of Resistance to Humid Atmospheres Containing Sulphur Dioxide).
Chromated aluminium panels painted with powders of formulation C are submitted to the acid humid atmosphere. One testcycle consists of 8 hours at 45°C and 2 litres of SO_2 followed by a 16 hours degassing at room temperature. After each testcycle the Δb^* -value is measured using a spectrophotometer with measuring geometry 0/45° and a D65-type illuminant. Using the CIE – L*a*b*-method, the b* -value is an indicator for blue/yellow colour variation. The green coloured powder paints (formulation C), containing Sicomin LS1522 (yellox pigment), upon exposure to acid conditions will turn to blue due to the destruction of the Sicomin LS1522,

becoming not well protected by the binder for the case the binder is insufficiently resistant to acid hydrolysis conditions.

An acid hydrolysis test takes 25 testcycles. The lower the Δb^* -value the more the binder system is resistant to acid hydrolysis conditions.

A binder system being sufficiently resistant to acid hydrolysis conditions proves a Δb^* -value of less than 5 after 25 testcycles.

Table 4

Cycle	Example 24	Crylcoat 440
0	0.00	0.00
1	0.25	0.25
2	0.49	0.48
3	0.71	0.65
4	0.94	0.78
5	1.09	0.96
6	1.21	1.08
7	1.63	1.20
8	1.84	1.19
9	2.10	1.29
10	2.20	1.41
11	1.95	1.37
12	2.04	1.42
13	2.17	1.55
14	2.55	1.61
15	2.58	1.63
16	2.95	1.60
17	2.83	1.63
18	3.01	1.63
19	3.12	1.68
20	3.14	1.66
21	3.09	1.75
22	3.32	1.82
23	3.47	1.92
24	3.56	1.87
25	3.51	2.01

CLAIMS:

1) Thermosetting binder compositions for powder coatings comprising a linear or branched carboxylic acid group containing isophtalic acid rich polyester, a linear or branched hydroxyl group containing polyester and a curing agent system having functional groups reactive with the polyester carboxylic acid groups and the hydroxyl groups, characterised in that the carboxylic group containing isophtalic acid rich polyester is amorphous and the hydroxyl group containing polyester is semi-crystalline.

2) Binder compositions according to claim 1, characterised in that the curing agent system is composed of at least one curing agent having functional groups reactive with the polyester carboxylic acid groups and at least one curing agent having functional groups reactive with the polyester hydroxyl groups, and/or at least one curing agent having functional groups reactive with both the polyester carboxylic acid groups and the polyester hydroxyl groups.

3) Binder composition according to anyone of the claims 1 and 2, characterised in that the carboxylic acid group containing amorphous polyester is composed of a dicarboxylic acid component comprising 50 to 100 mol percentage of isophthalic acid and from 0 to 50 mol percentage of another diacid selected from fumaric acid, maleic acid, phthalic anhydride, terephthalic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, succinic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azealic acid, sebacic acid, 1,12-dodecanedioic acid, etc., or the corresponding anhydrides., and of a glycol component comprising 70 to 100 mol percentage of neopentyl glycol and/or 2-butyl- 2-ethyl - 1,3-propanediol and 0 to 30 mol percentage of another glycol selected from ethyleneglycol, propyleneglycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 2-methyl 1,3-, hydrogenated Bisphenol A, hydroxypivalate of neopentyl glycol.

4) Binder composition according to anyone of the claims 1-3, characterised in that the carboxylic acid group containing amorphous polyester is a branched polyester incorporating up to 15 mol percentage relative to isophthalic acid, of a polyacid such as trimellitic acid, pyromellitic acid, etc, or their corresponding anhydrides.

5) Binder composition according to anyone of claims 1-3, characterised in that the carboxylic acid group containing amorphous polyester is a branched polyester

incorporating up to 15 mol percentage relative to neopentyl glycol and/or 2-butyl-2-ethyl-1,3-propanediol, of a polyol such as trimethylolpropane, ditrimethylolpropane, pentaerythrytol.

6) Binder composition according to anyone of the preceeding claims, characterised in that the hydroxyl functionalised semi-crystalline polyester is composed of 75 - 100 mol percentage of terephthalic acid and/or 1,4-cyclohexanedicarboxylic acid and from 0 to 25 mol percentage of another diacid selected from fumaric acid, maleic acid, phthalic anhydride, isophthalic acid, terephthalic acid, 1,4 cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, succinic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azealic acid, sebacic acid, 1,12-dodecanedioic acid, etc., and of a glycol component comprising from 75 to 100 mol percentage of an aliphatic non-branched diol selected from ethyleneglycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol 1,9-nonanediol, 1,10-decanediol, 14-tetradecanediol, 1,16-hexadecanediol, etc. used in a mixture or alone, and 0 to 25 mol percentage of another glycol selected from propyleneglycol, neopentyl glycol, 2-methyl-1,3-propanediol, 2-butyl,2-ethyl-1,3-propanediol, hydrogenated Bisphenol A, hydroxypivalate of neopentyl glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol.

7) Binder composition according to anyone of claims 1-5, characterised in that the hydroxyl functionalised semi-crystalline polyester is composed of 75 - 100 mol percentage of a linear non-branched aliphatic diacid selected from succinic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azealic acid, sebacic acid, 1,12-dodecanedioic acid, etc. used in a mixture or alone, and from 0 to 25 mol percentage of another diacid selected from fumaric acid, maleic acid, phthalic anhydride, terephthalic acid, isophthalic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, etc., and of a glycol component comprising from 75 to 100 mol percentage of a cycloaliphatic diol such as 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, hydrogenated Bisphenol A, etc. used in a mixture or alone, or an aliphatic non-branched diol such as ethyleneglycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6 hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 14-tetradecanediol, 1,16-hexadecanediol, etc. used in a mixture or alone, and from 0 to 25 mol percentage of another glycol selected from propyleneglycol,

neopentyl glycol, 2-methyl-1,3-, 2-butyl, 2-ethyl-1,3-propanediol, 1,4-cyclohexanediol, 1,4 cyclohexanedimethanol, hydrogenated Bisphenol A.

8) Binder composition according to anyone of claims 1-5, characterised in that the hydroxyl functionalised semi-crystalline polyester is a branched polyester incorporating up to 15 mol percentage based on the total of terephthalic acid, 1,4-cyclohexanedicarboxylic acid or non-branched aliphatic diacids, of a polyacid such as trimellitic acid, pyromellitic acid, etc., or their corresponding anhydrides.

9) Binder composition according to anyone of claims 1-5, characterised in that the hydroxyl functionalised semi-crystalline polyester is a branched polyester incorporating up to 15 mol percentage based on the total of aliphatic non-branched diols or cycloaliphatic diols, of a polyol such as trimethylolpropane, ditrimethylolpropane, pentaerythrytol.

10) Binder composition according to anyone of claims 1-5, characterised in that the hydroxyl functionalised semi-crystalline polyester is a branched polyester incorporating up to 30 mol percentage based on the total of terephthalic acid, 1,4-cyclohexanedicarboxylic acid or non-branched aliphatic diacids and/or on the total of aliphatic non-branched diols or cycloaliphatic diols, of monofunctional carboxylic acids having at least two hydroxyl groups wherein one or more of the hydroxyl groups can be hydroxyalkyl substituted, selected from α,α-bis-(hydroxymethyl)-propionic acid (dimethylolpropionic acid), α,α-bis-(hydroxymethyl)-butyric acid, α,α,α,-tris(bydroxymethyl)-acetic acid, α,α-bis-(hydroxymethyl)-valeric acid, α,α-bis-(hydroxy) propionic acid or α-phenylcarboxylic acids having at least two hydroxyl groups directly pendant to the phenyl ring (phenolic hydroxyl groups) such as 3,5-dihydroxybenzoic acid.

11) Binder composition according to anyone of the preceeding claims, characterised in that the carboxylic acid group containing isophthalic acid rich amorphous polyester has:

- an acid number from 15 to 100 mg KOH/g and preferably from 30 to 70 mg KOH/g;
- a number averaged molecular weight ranging from 1100 to 15000 and preferably from 1600 to 8500;
- a glass transition temperature (Tg) from 40 to 80°C ; and
- an ICI (cone/plate) viscosity at 200°C ranging from 5 to 15000 mPa.s

12) Binder composition according to anyone of the preceeding claims, characterised in that the hydroxyl group containing semi-crystalline polyester has:

- an hydroxyl number from 10 to 100 mg KOH/g and preferably from 15 to 80 mg KOH/g;
- a number averaged molecular weight ranging from 1100 to 17000 and preferably from 1400 to 11200;
- a fusion zone from 50 to 150°C;
- a glass transition temperature (Tg) from -50 to 50°C;
- a degree of crystallinity of at least 5 J/g and preferably 10J/g; and
- an ICI (cone/plate) viscosity at 175°C ranging from 5 to 10000 mPa.s

13) Binder composition according to anyone of the preceeding claims, characterised in that the thermosetting polyester blend is composed of :

- 55 to 95 and preferably 70 to 90 parts by weight of the carboxylic acid group containing isophthalic acid rich amorphous polyester; and
- 45 to 5 and preferably 30 to 10 parts by weight of the hydroxyl group containing semi-crystalline polyester.

14) Binder composition according to anyone of the preceeding claims, characterised in that the curing agent having functional groups reactive with the carboxylic acid groups of the isophthalic acid rich amorphous polyester, is a polyepoxy compound or a β-hydroxyalkylamide containing compound.

15) Binder composition according to anyone of the preceeding claims, characterised in that the curing agent having functional groups reactive with the hydroxyl groups of the semi-crystalline polyester, is a blocked polyisocyanate compound.

16) Binder composition according to anyone of the preceeding claims, characterised in that the carboxylic acid group containing amorphous polyester comprises a catalysing amount of thermosetting catalyst ranging from 0 to 5 weight percentage.

17) Binder composition according to anyone of the preceeding claims, characterised in that the hydroxyl group containing semi-crystalline polyester comprises a catalysing amount of thermosetting catalyst ranging from 0 to 5 weight percentage.

18) Binder composition according to anyone of the preceeding claims, characterised in that the binder is substantially based on:

- 28 to 93, preferably 43 to 86 parts by weight of the carboxylic acid group containing isophthalic acid rich amorphous polyester

- 43 to 3, preferably 29 to 7 parts by weight of the hydroxyl group containing semi-crystalline polyester
- 1 to 45, preferably 3 to 35 parts by weight of a curing agent having functional groups being reactive with the carboxylic acid groups of the amorphous polyester
- 21.0 to 0.1, preferably 9.0 to 0.5 parts by weight of a curing agent having functional groups reactive with the hydroxyl groups of the semi-crystalline polyester.

19) Thermosetting powder composition containing:

- a binder composition according to anyone of the preceeding claims
- UV-light absorbers and/or hindered amine light stabilisers
- flow control agent
- degassing agent.

20) Thermosetting powder composition according to claim 19 for use as a clear lacquer.

21) Thermosetting powder composition according to claim 19 containing pigments, dyes, fillers.

22) Entirely or partially coated substrate, characterised in that the coating material used, is a powder coating composition according to anyone of claims 19 to 21.

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2 5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 07 March 2001 (07.03.01)	
International application No. PCT/EP00/06063	**Applicant's or agent's file reference** 21.72.WO
International filing date (day/month/year) 29 June 2000 (29.06.00)	**Priority date** (day/month/year) 02 July 1999 (02.07.99)
Applicant MOENS, Luc, Ph., D. et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

18 January 2001 (18.01.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Juan Cruz

Telephone No.: (41-22) 338.83.38